JP 62-086,072

Job No.: 1505-93239 Ref.: JP 63-086072
Translated from Japanese by the Ralph McElroy Translation Company
910 West Avenue, Austin, Texas 78701 USA

JAPANESE PATENT OFFICE
PATENT JOURNAL (A)
KOKAI PATENT APPLICATION NO. SHO 62[1987]-86072

Int. Cl.[4]:	C 09 D 11/00 11/02 11/16
Sequence Nos. for Office Use:	A-7016-4J 7016-4J
Filing No.:	Sho 60[1985]-224903
Filing Date:	October 11, 1985
Publication Date:	April 20, 1987
No. of Inventions:	1 (Total of 6 pages)
Examination Request:	Not filed

WATER-BASED INK COMPOSITION

Inventors:

Suguru Shimada
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Kakuji Murakami
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Tamotsu Ariga
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Hiroyuki Kamimura
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Kiyofumi Nagai
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

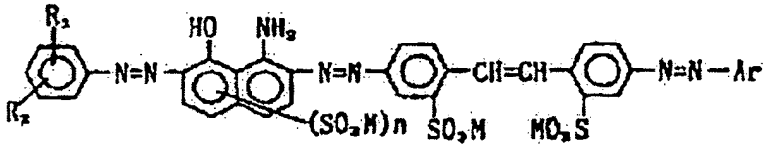
Applicant: Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Agents: Hitake Komatsu,
patent attorney, and 1 other

[There are no amendments to this patent.]

Claim

A water-based ink composition, characterized by including at least one kind of water-soluble dye represented by the following general formula:



R_1, R_2: Hydrogen, alkyl group, alkoxy group, halogen, cyano group, carboxyl group, sulfonate, hydroxyalkyl group, carbamoyl group, and sulfamoyl group
Ar: Phenyl group and naphthyl group substituted with, for example, a hydroxyl group, amino group, substituted amino group, alkyl group, and sulfonic acid group
M: Cation of hydrogen, sodium, potassium, lithium, organic amine, etc.
n = 1 or 2.

Detailed explanation of the invention

Field of the technology

The present invention pertains to a water-based ink composition suitable for printing, writing tools, recorders, and stamps. In particular, the present invention pertains to a black water-based ink composition having excellent performance for inkjet printing.

Prior art

In an inkjet recording, for good recording over a long period, the ink for use is required to meet the following conditions.

1) According to the liquid droplet generation method and liquid droplet ejection direction control method, the ink properties of viscosity, surface tension, specific conductivity, and density of the ink should be within an appropriate range.

2) During long-term storage, use over a long period, or a period of recording inactivity, no precipitation should occur by chemical changes, etc., and ink properties should not change.

3) A recorded image should have a sufficiently high contrast and should be sharp.

4) Drying of printed images should be fast.

In order to meet the above requirements, it is required that the molar absorption coefficient of the dye used in the ink be sufficiently high and the solubility of the dye in water and wetting agent be sufficiently high.

Furthermore, for ink used in a full color printer, etc., the following are required.

5) A hue with excellent purity should be exhibited.

6) The recorded image must be a sharp image with sufficient waterfastness, lightfastness, and wear resistance without blurring.

In order to meet the above requirements, a number of inks for inkjet recording have been proposed so far, however in actuality, inks that sufficiently meet all the above-mentioned conditions have not been obtained yet.

The above required characteristics depend on the materials prescribed in inks, especially the dye, and the development of a new dye has been in demand to meet these requirements.

Usually, a water-based ink composition is basically composed of a dye and a polyhydric alcohol called a wetting agent or its esters and water, and if necessary, additives such as antimicrobial agent are also included.

As dyes in a conventional black water-based ink, there are direct dyes and acid dyes such as C.I. Direct Black-4, -17, -19, -32, -38, -51, -75, -112, -154, etc., and C.I. Acid Black-1, -2, -7, -24, -28, -94, etc.

However, since the direct dyes among these have poor solubility, the image density and the contrast cannot be sufficiently raised by increasing their concentration.

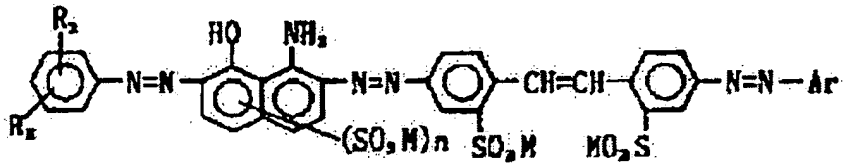
Also, although the acid dyes have good solubility, since the waterfastness of images is inferior, specially processed paper must be used.

Objective

The objective of the present invention is to provide a water-based ink composition in which the above-mentioned conventional drawbacks are solved. More specifically, the objective of the present invention is to provide a black water-based ink with excellent ejection characteristics, especially excellent image sharpness, waterfastness, and lightfastness, without clogging.

Constitution

The present inventors used a specific dye as a means to solve the above-mentioned drawbacks, and as a result, it was discovered that it had sufficient effects. Then, the present invention was completed. In other words, the water-based ink composition of the present invention is characterized by including at least one water-soluble dye represented by the following general formula.



R_1, R_2: Hydrogen, alkyl group, alkoxy group, halogen, cyano group, carboxyl group, sulfonate, hydroxyalkyl group, carbamoyl group, and sulfamoyl group

Ar: Phenyl group and naphthyl group substituted with, for example, hydroxyl group, amino group, substituted amino group, alkyl group, and sulfonic acid group

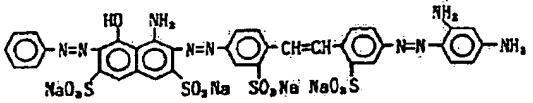
M: Cation of hydrogen, sodium, potassium, lithium, organic amine, etc.

n = 1 or 2.

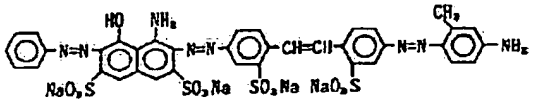
The content of the dye represented by the above-mentioned general formula is 0.5-20 parts by weight, preferably 1.5-6 parts by weight relative to the ink at 100 parts by weight. If the content is less than 0.5 part by weight, the effect as a colorant is weak, so that the hue of the image obtained is insufficient. If the content is more than 20 parts by weight (20 parts by weight are not included), precipitation occurs in the ink over the long term, so that inkjet recording tends to be insufficiently carried out.

Next, specific examples of said dyes are mentioned.

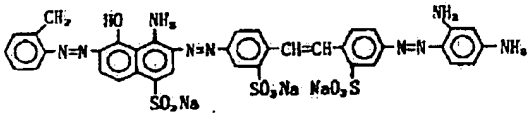
(1)



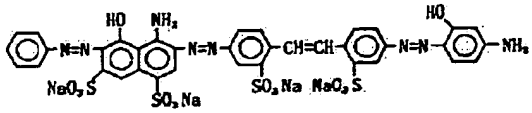
(2)



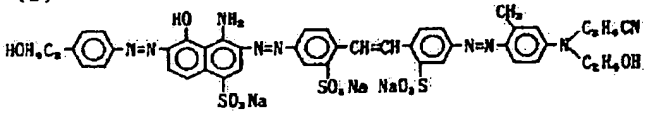
(3)



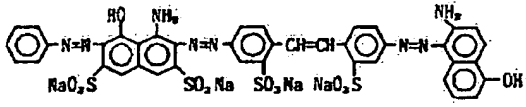
(4)



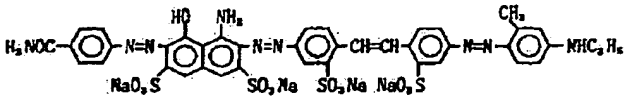
(5)



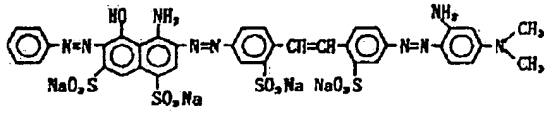
(6)



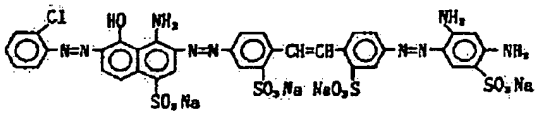
(7)



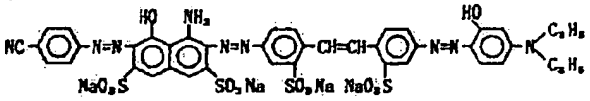
(8)



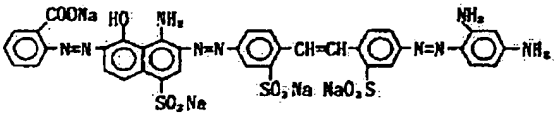
(9)



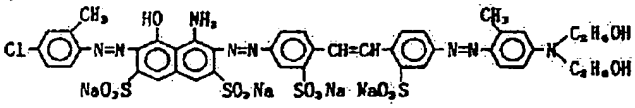
(10)



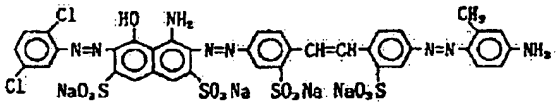
(11)



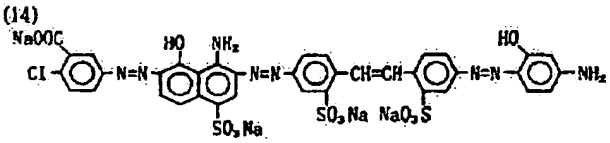
(12)



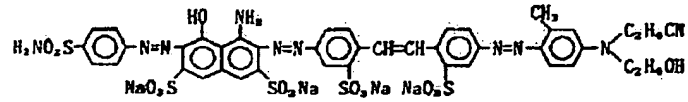
(13)



(14)



(15)



These dyes can be easily synthesized. For example, the dye shown in Specific Example (1), 3.7 g 4,4'-diaminostilbene-2,2'-disulfonic acid are tetraazotized with 1.5 g sodium nitrite in 100 mL water and 8 mL hydrochloric acid (10°C, 3 h). 3.6 g H acid and 150 mL water are added to the tetraazotized solution and reacted with sodium acetate at pH 3 for 8 h while being well stirred. Next, the reaction solution is alkalinized with sodium carbonate, and a diazotized solution of 1.0 g aniline is gradually added to it at 5°C or below to it and reacted for 1 h. Then, this solution is acidified, and 1.1 g m-phenylenediamine. pH is adjusted to 4-5 with sodium acetate and reacted at room temperature for 8 h. After the reaction is completed, it is salted out with table salt, so that 8.6 g black dye (yield 85%) with the structure shown by (1) are obtained.

The ink of the present invention uses water as the solvent component, and in order to adjust the ink properties to the desired values, to prevent the ink from drying, and to improve the solubility of the dye, the following water-soluble organic solvents can also be mixed with water and used.

Polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, and glycerin; alkyl ethers of polyhydric alcohols such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, and triethylene glycol monoethyl ether; N-methyl-2-pyrrolidone, 2-pyrrolidone, 1,3-dimethylimidazolidinone, dimethylformamide, triethanolamine, etc.

Among these, diethylene glycol, polyethylene glycol 200-600, triethylene glycol, ethylene glycol, glycerin, and N-methyl-2-pyrrolidone are especially preferable, and a high solubility of the dye and a clogging prevention effect due to preventing moisture evaporation can be obtained by using them.

The content of the above-mentioned water-soluble organic solvent in the ink can be in a range of 5-80% relative to the total ink weight, and the content is preferably in the range of 10-40% in terms of viscosity, dryness, etc.

In the ink of the present invention, conventional dyes and additives can be added in addition to the above-mentioned dyes and solvents.

As antiseptics and antimicrobial agents, sodium dehydroacetate, sodium sorbate, sodium 2-pyridinethiol-1-oxide, sodium benzoate, sodium pentachlorophenol, etc., can be used in the present invention.

As a pH adjustor, any substance can be used as long as the pH of the ink can be controlled within a range of 9.0-11.0 without having a negative influence on the ink being prepared.

As examples, amines such as diethanolamine and triethanolamine; hydroxides of alkali metal elements such as lithium hydroxide, sodium hydroxide, and potassium hydroxide; carbonate of alkali metals such as ammonium hydroxide [sic], lithium carbonate, sodium carbonate, and potassium carbonate, etc., are mentioned.

As a specific conductivity adjustor, for example, there are inorganic salts such as potassium chloride, ammonium chloride, sodium sulfate, and sodium carbonate, water-soluble amines such as triethanolamine, etc.

As a chelating agent, for example, there are sodium ethylenediaminetetraacetate, sodium nitrilotriacetate, sodium hydroxyethylethylenediaminetriacetate, sodium diethylenetriaminepentaacetate, sodium uramil diacetate, etc.

As an anticorrosion agent, for example, there are acidic [sic] sulfites, sodium thiosulfate, ammonium thioglycolate, diisopropylammonium nitrite, pentaerythritol tetranitrate, dicylcohexylammonium nitrite, etc.

In addition, water-soluble ultraviolet absorber water-soluble infrared absorber water-soluble high-molecular compound, dye dissolving acid, surfactant, etc., can be added in accordance with the purposes.

Next, application examples and comparative examples of the present invention are shown. % is wt%.

Application Example 1

The following composition was heated at about 50°C, stirred and dissolved, and filtered by a Teflon filter with a pore diameter of 0.22 μm, so that an ink was prepared. The properties of said ink are shown in Table 1.

Dye from Specific Example (1)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Similarly to Application Example 1 except for using materials of the following compositions, inks of Application Examples 2-5 and Comparative Examples 1-3 were prepared.

Application Example 2

Dye from Specific Example (5)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%

Water	76.8%
Application Example 3	
Dye from Specific Example (9)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%
Application Example 4	
Dye from Specific Example (12)	3.0%
Triethylene glycol	10.0%
2,2'-thiodiethanol	10.0%
Sodium benzoate	0.2%
Water	76.8%
Application Example 5	
Dye from Specific Example (15)	3.0%
Polyethylene glycol 200	5.0%
Triethylene glycol monomethyl ether	15.0%
Sodium benzoate	0.2%
Water	76.8%
Comparative Example 1	
Dye (C.I. Direct Black-32)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%
Comparative Example 2	
Dye (C.I. Direct Black-51)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%
Comparative Example 3	
Dye (C.I. Acid Black-28)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%

Water 76.8%

Table 1: Properties of inks

	pH (25℃)	粘度 (c.p.) (25℃) ①	表面張力 (dyne/cm) (25℃) ②	③ *1 耐水性 褪色率 (%)	③ *2 耐光性 褪色率 (%) ④
⑤ 実施例 1	9.9	2.02	53.2	5.7	2.6
〃 2	10.1	2.00	50.0	3.8	3.5
〃 3	10.2	1.98	53.8	5.6	1.7
〃 4	9.8	2.05	50.2	4.3	2.0
〃 5	9.8	2.08	51.0	5.0	3.2
⑥ 比較例 1	9.8	3.50	48.2	6.2	7.0
〃 2	10.2	2.82	52.0	7.6	3.7
〃 3	10.0	1.95	52.5	38.0	9.5

⑦ *1: インクを純水で染料濃度 1wt%に希釈して上質紙にドクターブレードで塗布し、1日風乾してサンプルを作成した。このサンプルを30℃の水に 1分間浸漬した後の濃度をマクベス濃度計で測定し浸漬前の濃度と比較した。

褪色率＝〔（浸漬前の濃度－浸漬後の濃度）／浸漬前の濃度〕×100

*2 *1と同様にして作成したサンプルを 3時間フェードメータ（カーボンアーク灯、63℃）にかけ*1と同じ方法で褪色率を求めた。

Key:
1 Viscosity (cP) (25°C)
2 Surface tension (dyne/cm) (25°C)
3 *1 Waterfastness, dye fading rate (%)
4 *2 Lightfastness, dye fading rate (%)
5 Application Example 1
6 Comparative Example 1
7 *1: The ink was diluted to a dye concentration of 1 wt% with purified water, spread on an individual sheet by a doctor blade, and dried for 1 day in the air, so that a sample was prepared. The sample was immersed for 1 min in water at 30°C, and the density [of the image] was measured by a Macbeth densitometer. It was compared with the density before immersion.
Dye fading rate: [(Density before immersion – Density after immersion)/ Density before immersion)] x 100
*2: A sample prepared similarly to *1 was applied to a Fade-0-Meter (carbon arc lamp, 63°C) for 3 h, and the dye fading rate was obtained by the same equation as *1.

Effect

(I) For the ink composition of Application Example 1, four items were evaluated and tested. The results are as follows.

1) Image sharpness and image dryness:

When the ink was jet-recorded on an individual commercially available sheet of paper under the condition of a particle frequency of 1100 kHz from a nozzle with an inner diameter of 30 μm, a sharp black image without blurring was obtained. The drying time of the recorded image was within 10 sec at normal temperature and normal humidity.

2) Shelf life

The ink was sealed in a glass container and stored at -20°C for 1 month, 4°C for 1 month, at 20°C for 1 year, and 90°C for 1 week, respectively. No precipitation was observed. No change was observed in the ink properties and the hue.

3) Ejection stability

The jet-recording of the above-mentioned 1) was continuously carried out for 1000 h, however no change was shown in nozzle clogging and ejection direction. Stable recording could be carried out.

4) Ejection responsivity

After jet-recording according to the above-mentioned 1), the ink was held at normal temperature and normal humidity for 1 month, at 40°C and 30% RH for 1 week, and jet-recording of 1) was carried out again. Similarly to the above-mentioned 3), stable recording could be carried out.

(II) For the inks of Application Examples 2-5, the ejection responsivity was tested in the same manner as that in Application Example 1. Good results similar to those of Application Example 1 were obtained. On the contrary, in Comparative Examples 1-3, when the inks were held at normal temperature and normal humidity for 1 week and 40°C and 30% RH for 3 days, partial clogging occurred in each nozzle, and the ink ejection direction was considerably unstable, so that jet recording was impossible.

JP 62-086,072

Job No.: 1505-93239 Ref.: JP 63-086072
Translated from Japanese by the Ralph McElroy Translation Company
910 West Avenue, Austin, Texas 78701 USA

JAPANESE PATENT OFFICE
PATENT JOURNAL (A)
KOKAI PATENT APPLICATION NO. SHO 62[1987]-86072

Int. Cl.[4]:	C 09 D 11/00 11/02 11/16
Sequence Nos. for Office Use:	A-7016-4J 7016-4J
Filing No.:	Sho 60[1985]-224903
Filing Date:	October 11, 1985
Publication Date:	April 20, 1987
No. of Inventions:	1 (Total of 6 pages)
Examination Request:	Not filed

WATER-BASED INK COMPOSITION

Inventors:

Suguru Shimada
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Kakuji Murakami
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Tamotsu Ariga
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Hiroyuki Kamimura
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Kiyofumi Nagai
Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

Applicant:

Ricoh Co., Ltd.
1-3-6 Nakaumagome
Ota-ku, Tokyo

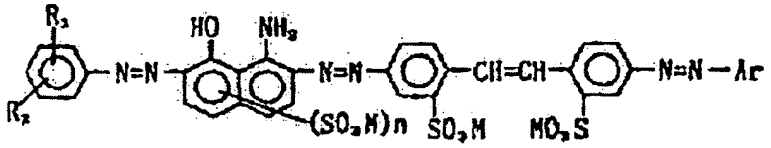
Agents:

Hitake Komatsu,
patent attorney, and 1 other

[There are no amendments to this patent.]

Claim

A water-based ink composition, characterized by including at least one kind of water-soluble dye represented by the following general formula:



R_1, R_2: Hydrogen, alkyl group, alkoxy group, halogen, cyano group, carboxyl group, sulfonate, hydroxyalkyl group, carbamoyl group, and sulfamoyl group
Ar: Phenyl group and naphthyl group substituted with, for example, a hydroxyl group, amino group, substituted amino group, alkyl group, and sulfonic acid group
M: Cation of hydrogen, sodium, potassium, lithium, organic amine, etc.
n = 1 or 2.

Detailed explanation of the invention

Field of the technology

The present invention pertains to a water-based ink composition suitable for printing, writing tools, recorders, and stamps. In particular, the present invention pertains to a black water-based ink composition having excellent performance for inkjet printing.

Prior art

In an inkjet recording, for good recording over a long period, the ink for use is required to meet the following conditions.

1) According to the liquid droplet generation method and liquid droplet ejection direction control method, the ink properties of viscosity, surface tension, specific conductivity, and density of the ink should be within an appropriate range.

2) During long-term storage, use over a long period, or a period of recording inactivity, no precipitation should occur by chemical changes, etc., and ink properties should not change.

3) A recorded image should have a sufficiently high contrast and should be sharp.

4) Drying of printed images should be fast.

In order to meet the above requirements, it is required that the molar absorption coefficient of the dye used in the ink be sufficiently high and the solubility of the dye in water and wetting agent be sufficiently high.

Furthermore, for ink used in a full color printer, etc., the following are required.

5) A hue with excellent purity should be exhibited.

6) The recorded image must be a sharp image with sufficient waterfastness, lightfastness, and wear resistance without blurring.

In order to meet the above requirements, a number of inks for inkjet recording have been proposed so far, however in actuality, inks that sufficiently meet all the above-mentioned conditions have not been obtained yet.

The above required characteristics depend on the materials prescribed in inks, especially the dye, and the development of a new dye has been in demand to meet these requirements.

Usually, a water-based ink composition is basically composed of a dye and a polyhydric alcohol called a wetting agent or its esters and water, and if necessary, additives such as antimicrobial agent are also included.

As dyes in a conventional black water-based ink, there are direct dyes and acid dyes such as C.I. Direct Black-4, -17, -19, -32, -38, -51, -75, -112, -154, etc., and C.I. Acid Black-1, -2, -7, -24, -28, -94, etc.

However, since the direct dyes among these have poor solubility, the image density and the contrast cannot be sufficiently raised by increasing their concentration.

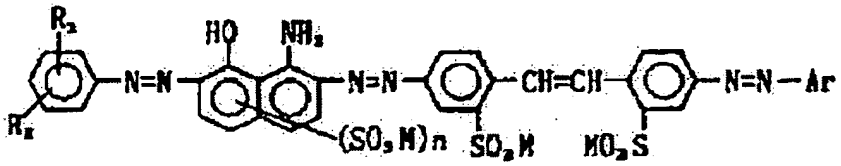
Also, although the acid dyes have good solubility, since the waterfastness of images is inferior, specially processed paper must be used.

Objective

The objective of the present invention is to provide a water-based ink composition in which the above-mentioned conventional drawbacks are solved. More specifically, the objective of the present invention is to provide a black water-based ink with excellent ejection characteristics, especially excellent image sharpness, waterfastness, and lightfastness, without clogging.

Constitution

The present inventors used a specific dye as a means to solve the above-mentioned drawbacks, and as a result, it was discovered that it had sufficient effects. Then, the present invention was completed. In other words, the water-based ink composition of the present invention is characterized by including at least one water-soluble dye represented by the following general formula.



R_1, R_2: Hydrogen, alkyl group, alkoxy group, halogen, cyano group, carboxyl group, sulfonate, hydroxyalkyl group, carbamoyl group, and sulfamoyl group

Ar: Phenyl group and naphthyl group substituted with, for example, hydroxyl group, amino group, substituted amino group, alkyl group, and sulfonic acid group

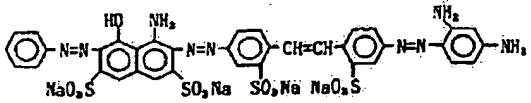
M: Cation of hydrogen, sodium, potassium, lithium, organic amine, etc.

n = 1 or 2.

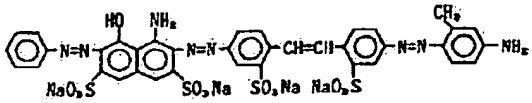
The content of the dye represented by the above-mentioned general formula is 0.5-20 parts by weight, preferably 1.5-6 parts by weight relative to the ink at 100 parts by weight. If the content is less than 0.5 part by weight, the effect as a colorant is weak, so that the hue of the image obtained is insufficient. If the content is more than 20 parts by weight (20 parts by weight are not included), precipitation occurs in the ink over the long term, so that inkjet recording tends to be insufficiently carried out.

Next, specific examples of said dyes are mentioned.

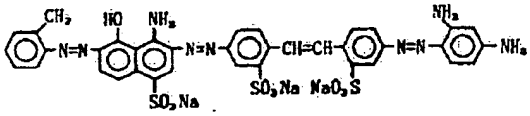
(1)



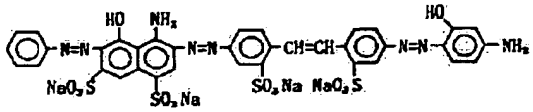
(2)



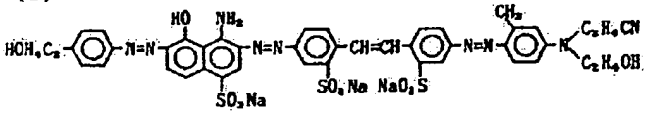
(3)



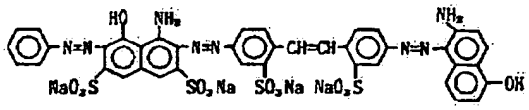
(4)



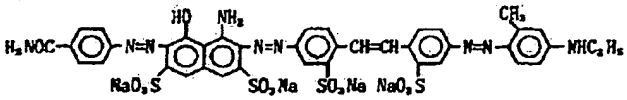
(5)



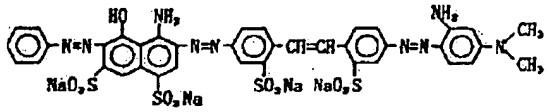
(6)



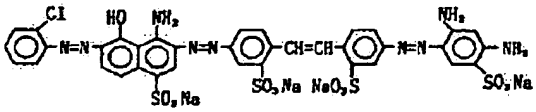
(7)



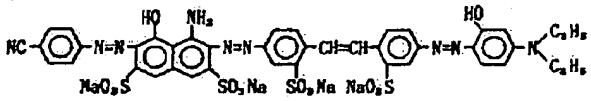
(8)



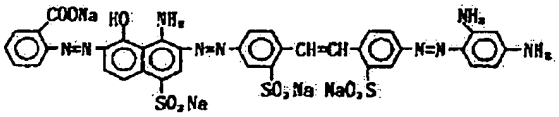
(9)



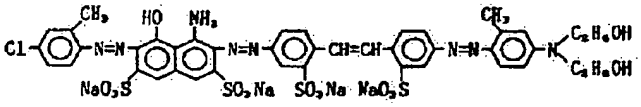
(10)



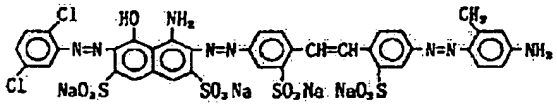
(11)



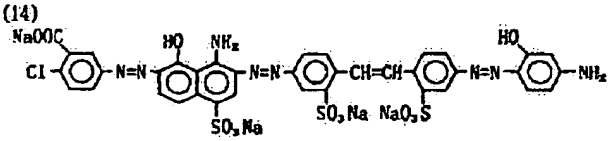
(12)



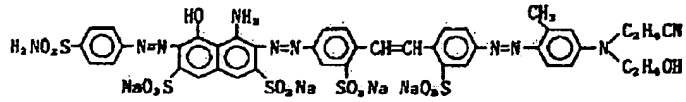
(13)



(14)



(15)



These dyes can be easily synthesized. For example, the dye shown in Specific Example (1), 3.7 g 4,4'-diaminostilbene-2,2'-disulfonic acid are tetraazotized with 1.5 g sodium nitrite in 100 mL water and 8 mL hydrochloric acid (10°C, 3 h). 3.6 g H acid and 150 mL water are added to the tetraazotized solution and reacted with sodium acetate at pH 3 for 8 h while being well stirred. Next, the reaction solution is alkalinized with sodium carbonate, and a diazotized solution of 1.0 g aniline is gradually added to it at 5°C or below to it and reacted for 1 h. Then, this solution is acidified, and 1.1 g m-phenylenediamine. pH is adjusted to 4-5 with sodium acetate and reacted at room temperature for 8 h. After the reaction is completed, it is salted out with table salt, so that 8.6 g black dye (yield 85%) with the structure shown by (1) are obtained.

The ink of the present invention uses water as the solvent component, and in order to adjust the ink properties to the desired values, to prevent the ink from drying, and to improve the solubility of the dye, the following water-soluble organic solvents can also be mixed with water and used.

Polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, and glycerin; alkyl ethers of polyhydric alcohols such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, and triethylene glycol monoethyl ether; N-methyl-2-pyrrolidone, 2-pyrrolidone, 1,3-dimethylimidazolidinone, dimethylformamide, triethanolamine, etc.

Among these, diethylene glycol, polyethylene glycol 200-600, triethylene glycol, ethylene glycol, glycerin, and N-methyl-2-pyrrolidone are especially preferable, and a high solubility of the dye and a clogging prevention effect due to preventing moisture evaporation can be obtained by using them.

The content of the above-mentioned water-soluble organic solvent in the ink can be in a range of 5-80% relative to the total ink weight, and the content is preferably in the range of 10-40% in terms of viscosity, dryness, etc.

In the ink of the present invention, conventional dyes and additives can be added in addition to the above-mentioned dyes and solvents.

As antiseptics and antimicrobial agents, sodium dehydroacetate, sodium sorbate, sodium 2-pyridinethiol-1-oxide, sodium benzoate, sodium pentachlorophenol, etc., can be used in the present invention.

As a pH adjustor, any substance can be used as long as the pH of the ink can be controlled within a range of 9.0-11.0 without having a negative influence on the ink being prepared.

As examples, amines such as diethanolamine and triethanolamine; hydroxides of alkali metal elements such as lithium hydroxide, sodium hydroxide, and potassium hydroxide; carbonate of alkali metals such as ammonium hydroxide [sic], lithium carbonate, sodium carbonate, and potassium carbonate, etc., are mentioned.

As a specific conductivity adjustor, for example, there are inorganic salts such as potassium chloride, ammonium chloride, sodium sulfate, and sodium carbonate, water-soluble amines such as triethanolamine, etc.

As a chelating agent, for example, there are sodium ethylenediaminetetraacetate, sodium nitrilotriacetate, sodium hydroxyethylethylenediaminetriacetate, sodium diethylenetriaminepentaacetate, sodium uramil diacetate, etc.

As an anticorrosion agent, for example, there are acidic [sic] sulfites, sodium thiosulfate, ammonium thioglycolate, diisopropylammonium nitrite, pentaerythritol tetranitrate, dicylcohexylammonium nitrite, etc.

In addition, water-soluble ultraviolet absorber water-soluble infrared absorber water-soluble high-molecular compound, dye dissolving acid, surfactant, etc., can be added in accordance with the purposes.

Next, application examples and comparative examples of the present invention are shown. % is wt%.

Application Example 1

The following composition was heated at about 50°C, stirred and dissolved, and filtered by a Teflon filter with a pore diameter of 0.22 μm, so that an ink was prepared. The properties of said ink are shown in Table 1.

Dye from Specific Example (1)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Similarly to Application Example 1 except for using materials of the following compositions, inks of Application Examples 2-5 and Comparative Examples 1-3 were prepared.

Application Example 2

Dye from Specific Example (5)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%

Water	76.8%
Application Example 3	
Dye from Specific Example (9)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%
Application Example 4	
Dye from Specific Example (12)	3.0%
Triethylene glycol	10.0%
2,2'-thiodiethanol	10.0%
Sodium benzoate	0.2%
Water	76.8%
Application Example 5	
Dye from Specific Example (15)	3.0%
Polyethylene glycol 200	5.0%
Triethylene glycol monomethyl ether	15.0%
Sodium benzoate	0.2%
Water	76.8%
Comparative Example 1	
Dye (C.I. Direct Black-32)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%
Comparative Example 2	
Dye (C.I. Direct Black-51)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%
Comparative Example 3	
Dye (C.I. Acid Black-28)	3.0%
Diethylene glycol	15.0%
Glycerin	5.0%
Sodium dehydroacetate	0.2%

Water 76.8%

Table 1: Properties of inks

	pH (25℃)	粘度 (c.p.) (25℃) ①	表面張力 (dyne/cm) (25℃) ②	③ *1 耐水性 褪色率 (%)	③ *2 耐光性 褪色率 (%) ④
⑤ 実施例1	9.9	2.02	53.2	5.7	2.6
〃 2	10.1	2.00	50.0	3.8	3.5
〃 3	10.2	1.98	53.8	5.6	1.7
〃 4	9.8	2.05	50.2	4.3	2.0
〃 5	9.8	2.08	51.0	5.0	3.2
⑥ 比較例1	9.8	3.50	48.2	6.2	7.0
〃 2	10.2	2.82	52.0	7.6	3.7
〃 3	10.0	1.95	52.5	38.0	9.5

⑦ *1: インクを純水で染料濃度 1wt%に希釈して上質紙にドクターブレードで塗布し、1日風乾してサンプルを作成した。このサンプルを30℃の水に 1分間浸漬した後の濃度をマクベス濃度計で測定し浸漬前の濃度と比較した。

褪色率＝〔（浸漬前の濃度－浸漬後の濃度）／浸漬前の濃度〕×100

*2 *1と同様にして作成したサンプルを 3時間フェードメータ（カーボンアーク灯、63℃）にかけ*1と同じ方法で褪色率を求めた。

Key: 1 Viscosity (cP) (25°C)
2 Surface tension (dyne/cm) (25°C)
3 *1 Waterfastness, dye fading rate (%)
4 *2 Lightfastness, dye fading rate (%)
5 Application Example 1
6 Comparative Example 1
7 *1: The ink was diluted to a dye concentration of 1 wt% with purified water, spread on an individual sheet by a doctor blade, and dried for 1 day in the air, so that a sample was prepared. The sample was immersed for 1 min in water at 30°C, and the density [of the image] was measured by a Macbeth densitometer. It was compared with the density before immersion.
Dye fading rate: [(Density before immersion – Density after immersion)/ Density before immersion)] x 100
*2: A sample prepared similarly to *1 was applied to a Fade-0-Meter (carbon arc lamp, 63°C) for 3 h, and the dye fading rate was obtained by the same equation as *1.

Effect

(I) For the ink composition of Application Example 1, four items were evaluated and tested. The results are as follows.

1) Image sharpness and image dryness:

When the ink was jet-recorded on an individual commercially available sheet of paper under the condition of a particle frequency of 1100 kHz from a nozzle with an inner diameter of 30 μm, a sharp black image without blurring was obtained. The drying time of the recorded image was within 10 sec at normal temperature and normal humidity.

2) Shelf life

The ink was sealed in a glass container and stored at -20°C for 1 month, 4°C for 1 month, at 20°C for 1 year, and 90°C for 1 week, respectively. No precipitation was observed. No change was observed in the ink properties and the hue.

3) Ejection stability

The jet-recording of the above-mentioned 1) was continuously carried out for 1000 h, however no change was shown in nozzle clogging and ejection direction. Stable recording could be carried out.

4) Ejection responsivity

After jet-recording according to the above-mentioned 1), the ink was held at normal temperature and normal humidity for 1 month, at 40°C and 30% RH for 1 week, and jet-recording of 1) was carried out again. Similarly to the above-mentioned 3), stable recording could be carried out.

(II) For the inks of Application Examples 2-5, the ejection responsivity was tested in the same manner as that in Application Example 1. Good results similar to those of Application Example 1 were obtained. On the contrary, in Comparative Examples 1-3, when the inks were held at normal temperature and normal humidity for 1 week and 40°C and 30% RH for 3 days, partial clogging occurred in each nozzle, and the ink ejection direction was considerably unstable, so that jet recording was impossible.

⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　昭62－86072

⑤Int.Cl.⁴	識別記号	庁内整理番号	㊸公開　昭和62年(1987)4月20日
C 09 D 11/00	101		
	PSZ	A－7016－4J	
11/02	PTF	7016－4J	
11/16	PTZ	7016－4J	審査請求　未請求　発明の数 1　（全6頁）

㊹発明の名称　水性インク組成物

㉑特　願　昭60－224903

㉒出　願　昭60(1985)10月11日

㉒発明者　島田　勝　東京都大田区中馬込1丁目3番6号　株式会社リコー内

㉒発明者　村上　格二　東京都大田区中馬込1丁目3番6号　株式会社リコー内

㉒発明者　有賀　保　東京都大田区中馬込1丁目3番6号　株式会社リコー内

㉒発明者　上村　浩之　東京都大田区中馬込1丁目3番6号　株式会社リコー内

㉒発明者　永井　希世文　東京都大田区中馬込1丁目3番6号　株式会社リコー内

㉑出願人　株式会社リコー　東京都大田区中馬込1丁目3番6号

㉔代理人　弁理士　小松　秀岳　外1名

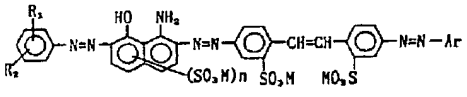
明細書

1．発明の名称

水性インク組成物

2．特許請求の範囲

下記一般式で表わされる水溶性染料を少なくとも一種含有することを特徴とする水性インク組成物。



R_1、R_2：水素、アルキル基、アルコキシ基、ハロゲン、シアノ基、カルボキシル基、スルホン酸基、ヒドロキシアルキル基、カルバモイル基、スルファモイル基

Ar：水酸基、アミノ基、置換アミノ基、アルキル基、スルホン酸基等の置換基を有するフェニル基およびナフチル基

M：水素、ナトリウム、カリウム、リチウム、有機アミン等のカチオンを示す。

n＝1または2。

3．発明の詳細な説明

技術分野

本発明は印刷用、筆記具用、記録計用、スタンプ用として好適な水性インク組成物に関するものであり、特にインクジェット印刷用としてすぐれた性能を有する黒色水性インク組成物に関する。

従来技術

インクジェット記録において、長時間に亘って良好な記録を行なうためには、使用するインクが以下の条件を満たすことが必要である。

1）液滴発生方法や液滴飛翔方向制御方法に応じたインク物性として、インクの粘度、表面張力、比電導度、密度が適正範囲に含まれること。

2）長期間保存、長期間使用あるいは記録休止中に化学変化などにより析出が生じたり、イ

ンク物性値が変化してはならないこと。

3) 記録される画像が充分にコントラストが高く、鮮明であること。

4) 印字画像の乾燥が速いこと。

以上の要求を満たすためには、インクに使用する染料の分子吸光係数が十分に高いこと、染料の水および湿潤剤に対する溶解度が十分に高いことが要求される。

更にフルカラー・プリンター等に用いられるインクには

5) 色調に優れた色調を示すこと。また、

6) 記録された画像は当然のこととして耐水性、耐光性、耐摩耗性に富むニジミのない鮮明画像でなければならないこと。

以上のような要求を満足するためこれまでに、インクジェット記録用インクとして幾多の提案がなされているが、上記の諸条件のすべてを充分に満足するものはいまだに得られていないのが現状である。

以上に要求される特性は、インクに処方される材料の中で特に染料により左右されるものであり、これらの要求を満足するために、新規な染料の開発が待たれていた。

通常、水性インク組成物は、基本的には、染料及び湿潤剤といわれる多価アルコールまたはそのエーテル類と水とより構成され、必要に応じてさらに防カビ剤等の添加剤を含有するものである。

従来の黒色水性インクにおいて染料としてはC.I.ダイレクトブラック-1、-17、-19、-32、-38、-51、-75、-112、-154等やC.I.アシッドブラック-1、-2、-7、-24、-28、-94等の直接染料や酸性染料がある。

しかしながら、これらの染料のうち直接染料は溶解性が悪いことから、その含有濃度を増大して画像濃度、コントラストを充分に上げることができない。

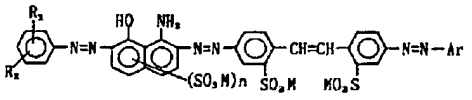
また酸性染料は溶解性は良いものの特に画像の耐水性に劣るため特殊な加工紙を使用しなければならない。

目　的

本発明は、上記従来の欠点を解決した水性インク組成物を提供するものであり、より詳細には吸射特性がすぐれて目詰まりがなく、特に画像の鮮明性、耐水性、耐光性にすぐれた黒色水性インクを提供するものである。

構　成

本発明者は、上記欠点を解決する手段として特定の染料を用いることが、十分な効果をもたらすことを見い出して、本発明にいたった。すなわち、本発明のインク組成物は、下記一般式で表わされる水溶性染料を少なくとも一種含有することを特徴とするものである。



R_1、R_2：水素、アルキル基、アルコキシ基、ハロゲン、シアノ基、カルボキシル基、スルホン酸基、ヒドロキシアルキル基、カルバモイル基、スルファモイル基

Ar：水酸基、アミノ基、置換アミノ基、アルキル基、スルホン酸基等の置換基を有するフェニル基およびナフチル基

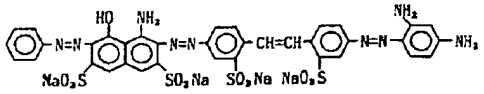
M：水素、ナトリウム、カリウム、リチウム、有機アミン等のカチオンを示す。

n＝1または2。

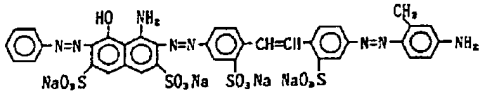
上記一般式で表わされる染料の含有量は、インク100重量部に対して0.5～20重量部、好ましくは1.5～6重量部が適当である。0.5重量部未満であると着色剤としての効力がうすれて、得られる画像の色調は不十分となり、また20重量部以上（20重量部は含まない）の場合には長時間経時させるとインク中に析出が生じてインクジェット記録が十分に行なわれなくなる傾向がある。

以下に該染料の具体例を列挙する。

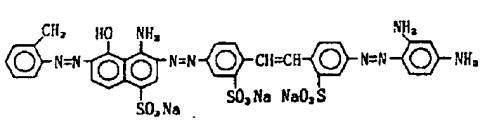
(1)



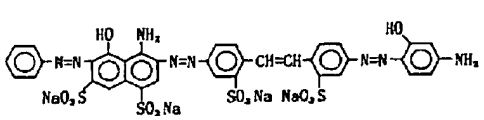
(2)



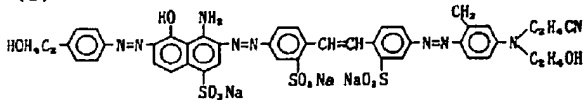
(3)



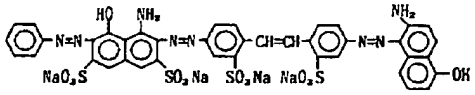
(4)



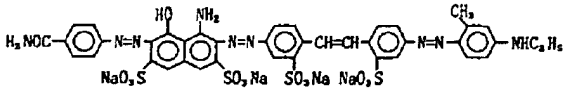
(5)



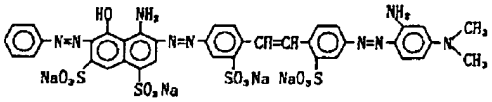
(6)



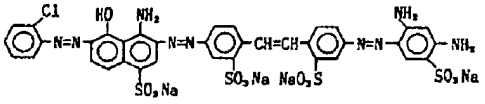
(7)



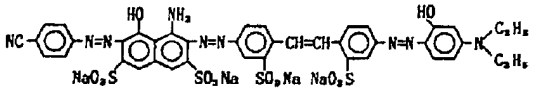
(8)



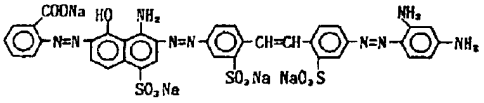
(9)



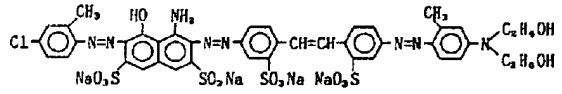
(10)



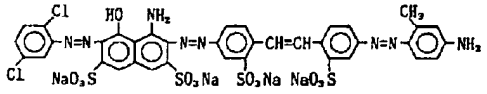
(11)



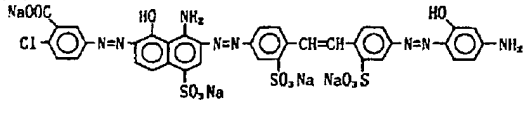
(12)



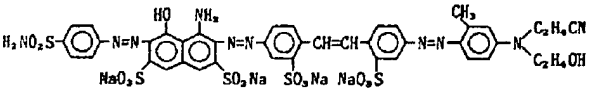
(13)



(14)



(15)



これらの染料は容易に合成することができる。例えば具体例(1)で示される染料は 3.7g の 4,4′-ジアミノスチルベン-2,2′-ジスルホン酸を水 100ml、塩酸 8ml中で亜硝酸ソーダ 1.5g にてテトラゾ化する（10℃、3時間）。このテトラゾ化液にH酸 3.6g、水 150mlを加えてよく撹拌しながら酢酸ソーダで pH 3として 8時間反応する。次にこの反応液を炭酸ソーダでアルカリ性とし、5℃以下でアニリン 1.0g のジアゾ化液を少しづつ加え 1時間反応する。そしてこの液を再び酸性とし、メタフェニレンジアミン 1.1g を加える。酢酸ソーダで pHを 4～5 とし室温で 8時間反応する。終了後食塩で塩析し、(1)で示される褐色の黒色染料 8.6g（収率85%）を得た。

本発明のインクは、溶媒成分として水を使用するものであるが、インク物性を所望の値に調整するため、インクの乾燥を防止するため、染料の溶解性を向上するため等の目的で、下記の水溶性有機溶媒と水とを混合して使用すること

もできる。

エチレングリコール、ジエチレングリコール、トリエチレングリコール、ポリエチレングリコール、ポリプロピレングリコール、グリセリン等の多価アルコール類、エチレングリコールモノエチルエーテル、エチレングリコールモノブチルエーテル、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノエチルエーテル、ジエチレングリコールモノブチルエーテル、トリエチレングリコールモノメチルエーテル、トリエチレングリコールモノエチルエーテル等の多価アルコールのアルキルエーテル類、その他、N－メチル－2－ピロリドン、2－ピロリドン、1,3－ジメチルイミダゾリジノン、ジメチルホルムアミド、トリエタノールアミン等である。

これらの中で特に好ましいのはジエチレングリコール、ポリエチレングリコール200～600、トリエチレングリコール、エチレングリコール、グリセリン、N－メチル－2－ピロリドンであり、これらを用いることにより染料の高い溶解性と水分蒸発防止による目詰り防止の効果を得ることが出来る。

インク中の上記水溶性有機溶媒の含有量はインク全重量に対して5～80%の範囲で使用できるが、粘性、乾燥性等から10～40%の範囲で用いることが好ましい。

本発明のインクには上記染料、溶剤の他に従来より知られている染料および添加剤を加えることができる。

防腐防黴剤としては、デヒドロ酢酸ソーダ、ソルビン酸ソーダ、2－ピリジンチオール－1－オキサイドナトリウム、安息香酸ナトリウム、ペンタクロロフェノールナトリウム等が本発明に使用できる。

pH調整剤としては、調合されるインクに悪影響をおよぼさずに、インクのpHを9.0～11.0の範囲に制御できるものであれば任意の物質を使用することができる。

その例として、ジエタノールアミン、トリエタノールアミンなどのアミン、水酸化リチウム、水酸化ナトリウム、水酸化カリウムなどのアルカリ金属元素の水酸化物、水酸化アンモニウム、炭酸リチウム、炭酸ナトリウム、炭酸カリウムなどのアルカリ金属の炭酸塩などがあげられる。

比電気伝導度調整剤としては、例えば、塩化カリウム、塩化アンモニウム、硫酸ナトリウム、炭酸ナトリウムなどの無機塩、トリエタノールアミンなどの水溶性アミンなどがある。

キレート試薬としては、例えば、エチレンジアミン四酢酸ナトリウム、ニトリロ三酢酸ナトリウム、ヒドロオキシエチルエチレンジアミン三酢酸ナトリウム、ジエチレントリアミン五酢酸ナトリウム、ウラミル二酢酸ナトリウムなどがある。

防錆剤としては、例えば、酸性亜硫酸塩、チオ硫酸ナトリウム、チオグリコール酸アンモン、ジイソプロピルアンモニウムニトライト、四硝酸ペンタエリスリトール、ジシクロヘキシルアンモニウムニトライトなどがある。

その他目的に応じて、水溶性紫外線吸収剤、水溶性赤外線吸収剤、水溶性高分子化合物、染料溶解剤、界面活性剤などを添加することができる。

以下に本発明の実施例および比較例を示す。%はすべて重量%である。

実施例1

下記の組成物を約50℃に加熱して撹拌溶解した後、孔径0.22μmのテフロンフィルターで濾過することによってインクを作成した。該インクの物性は表－1に示すとおりである。

具体例(1)の染料	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

下記の組成よりなる材料を用いる以外は実施例1と同様にして、実施例2～5、および比較例1～3のインクを作成した。

実施例2

具体例(5)の染料	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

実施例3

具体例(9)の染料	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

実施例4

具体例(2)の染料	3.0%
トリエチレングリコール	10.0%
2,2′－チオジエタノール	10.0%
安息香酸ナトリウム	0.2%
水	76.8%

実施例5

具体例(5)の染料	3.0%
ポリエチレングリコール 200	5.0%
トリエチレングリコールモノメチルエーテル	15.0%
安息香酸ナトリウム	0.2%
水	76.8%

比較例1

染料（C．I．ダイレクトブラック32）	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

比較例2

染料（C．I．ダイレクトブラック51）	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

比較例3

染料（C．I．アシッドブラック28）	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

表－1　インクの物性

	pH (25℃)	粘度 (c.p.) (25℃)	表面張力 (dyne/cm) (25℃)	※1 耐水性 褪色率 (%)	※2 耐光性 褪色率 (%
実施例1	9.9	2.02	53.2	5.7	2.6
〃 2	10.1	2.00	50.0	3.8	3.5
〃 3	10.2	1.98	53.8	5.6	1.7
〃 4	9.8	2.05	50.2	4.3	2.0
〃 5	9.8	2.08	51.0	5.0	3.2
比較例1	9.8	3.50	48.2	6.2	7.0
〃 2	10.2	2.82	52.0	7.6	3.7
〃 3	10.0	1.95	52.5	38.0	9.5

※1　インクを純水で染料濃度 1wt%に希釈して上質紙にドクターブレードで塗布し、1日風乾してサンプルを作成した。このサンプルを30℃の水に 1分間浸漬した後の濃度をマクベス濃度計で測定し浸漬前の濃度と比較した。

褪色率＝〔（浸漬前の濃度－浸漬後の濃度）／浸漬前の濃度〕×100

※2　※1と同様にして作成したサンプルを 3時間フェードメータ（カーボンアーク灯、63℃）にかけ※1と同じ方法で褪色率を求めた。

効　果

（I）実施例1のインク組成物について、4つの項目について評価試験を行った。その結果を以下に示す。

1）画像鮮明性および画像の乾燥性：

内径30μmのノズルから粒子周波数1100kHzの条件で市場の上質紙上にインクをジェット記録したところ、ニジミのない鮮明な黒色画像が得られた。記録物の乾燥時間は常温常湿で10秒以内であった。

2）保存性：

インクをガラス容器に密閉し、－20℃で1カ月間、4℃で1カ月間、20℃で1年間、及び90℃で1週間、夫々保存したが、析出は認められなかった。またインク物性や色調についても変化は認められなかった。

3）噴射安定性：

前記1）のジェット記録を1000時間連続して行なったが、ノズルに目詰りや噴射方向の変化なく、安定した記録が行なえた。

4）噴射応答性：

前記 1）に従ってジェット記録を行なった後、常温常湿で 1カ月間、及び40℃－30％ＲＨで 1週間夫々放置し、ついで再び 1）のジェット記録を行なったが、前記 3）と同様、安定した記録が行なえた。

（Ⅱ）実施例２～５のインクについて実施例１と同じく噴射応答性をテストしたところ実施例１と同様に良好な結果が得られた。これに対して比較例１～３の場合は、常温常湿で 1週間、および40℃30％ＲＨで 3日間放置したところ、各々ノズルの部分的目詰りが生じてインクの噴射方向が著しく不安定となり、ジェット記録は不可能であった。

特許出願人　株式会社リコー
代理人　弁理士　小松秀岳
代理人　弁理士　旭　宏